Investigating the Growth Behavior of LDH Layers on MAO-coated Aluminum Alloy: Influence of Microstructure and Surface Element

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Layered double hydroxide (LDH) layers were grown *in-situ* on the surface of micro-arc oxidation (MAO) ceramic coating applied on 2024 aluminum alloy. It was found that the microstructure and surface element of MAO film have a significant effect on the growth behavior of LDH layers. In the initial stage of growth, LDHs grains can be preferentially formed in/on the micro-pores/-cracks of MAO coating to provide effective film repairs. However, some surface regions on MAO coating were not still covered by the LDH layers after long time of growth. The results showed that the content of Si element was higher in the regions without LDH nanoplatelets growth. Therefore, we use two approaches to investigate influence of surface Si element on the growth behavior of LDH layers on MAO coating: one is to replace the Na_2SiO_4 electrolyte to $NaAlO_2$ electrolyte used in the MAO process, removing the content of Si on the surface of MAO coating; another is to polish the MAO coating, reducing the enriched Si elements of the outer layer. After removing of surface Si, the LDH layers were uniformly and completely covered on the surface of MAO coating during the growth process. The results demonstrate that the distribution of Si element on the MAO surface significantly inhibit the nucleation and growth of LDH grains.

1. INTRODUCTION

Aluminum and its alloys are widely used in aerospace, military and civil areas because of their light weight, high specific strength and good thermal conductivity. However, the poor corrosion resistance has limited its further application [1-4]. Micro-arc oxidation (MAO) is an ideal technology

for aluminum alloy protection, which has the advantages of low price, environmental protection and simple process. However, there are a lot of micro-pores and micro-cracks due to the intensive and continual sparking discharge and the thermal stress generated in the formed MAO coating. Discharge holes and micro-cracks on the surface of the coating are the key factors influencing the coating corrosion resistance [5-7]. Therefore, the MAO coating needs to be composite in order to further improve the corrosion resistance of aluminum alloy.

Layered double hydroxides (LDHs) have been used in the field of metal protection based on its special structural advantages, and becoming a new and efficient intelligent protection material. LDHs is a kind of anionic layered structure material, thus can be used as a "nanocontainer" for loading and controlling release corrosion inhibitors [8-10]. LDH layers, which directly prepared on the surface of metal materials, are able to provide the whole layer becoming a "container" loading corrosion inhibitor. When it is exposed to corrosive ions (such as Cl^-) in the environmental medium, LDHs layers can release inhibitor anions in the layers and capture the Cl^- by the ion exchange property, providing an active long-term protection. The in-situ growth method is a controllable preparation method of LDHs layer materials. The prepared layers have strong adhesion with substrate and controllable crystal orientation [11-12]. At present, there have been studies of in-situ growth of LDHs layers on aluminum alloy, anodic oxide coatings and micro-arc oxidation coatings. Wang et al. [13] demonstrated that the corrosion resistance of hydrotalcite coating was enhanced by the chemical modification of the coating with 8-hydroxyquinolate anions. Kuznetsov et al. [14] have reported that the LDH layer can be used as "smart" nanocontainers when loaded with anionic corrosion inhibitors (vanadates) applied on TSA anodized 2024 aluminum alloy, showing an effective enhancement of corrosion resistance by corrosion inhibitors. Duan et al. first used in-situ growth method to prepare "nest" films on anodized aluminum sheet (PAO/Al) [15]. Then, the organic/inorganic ZnAl-La LDHs/PAO hybrid film with super-hydrophobic and high adhesion was prepared by intercalating the lauric acid (La^-) into the LDHs layer based on the ion exchange characteristics of NO_3^- type LDHs [16,17]. In addition, they also explain the growth mechanism of NiAl LDHs and ZnAl LDHs on PAO/Al substrates, respectively [18]. They found that the growth process of NiAl and ZnAl LDH films followed the heterogeneous nucleation and homogeneous nucleation mechanism, respectively. Ding et al. [19] investigated the effect of divalent ions (Ni^{2+}, Zn^{2+}, Mg^{2+} and Cu^{2+}) on the growth behavior of LDH on AAO surface. It was found that different ion types had a significant effect on LDH crystal growth, which directly caused the structure and morphological differences. Li et al. [20] prepared LDH layers on the surface of anodic aluminum alloy and discussed the effect of sealing treatment on the growth of LDHs. Compared with hydrated aluminum hydroxide, anodic alumina has higher reactivity, which is more conducive to the crystallization and growth of LDH layer.

Our research group [21] has fabricated LDH layers in situ on the surface of MAO-coated aluminum alloy, and researching on the corrosion resistance of composite film with corrosion inhibitor. However, the growth of LDH layers on the surface of MAO coating needs to be further discussed. In this paper, we have investigated the influence of MAO coating on the growth behavior of LDH layers, and analyzed its influence factors focusing on microstructure and element content of MAO coating.

2. EXPERIMENT

2.1 Preparation of MAO ceramic layer

2024 aluminum alloy plates (30 mm × 30 mm × 3 mm) were degreased by ultrasonication in ethanol, and then rinsed with deionized water, alkaline cleaning (50 g/L NaOH) at 60 °C for 15 min, desmutting (20% HNO_3) at 25 °C for 30 s, finally dried in air. The specimens were respectively treated in electrolytes solution of 18 g/L $Na_2SiO_3$and 9 g/L KOH and 18 g/L $NaAlO_2$and 9 g/L KOH at 25 °C for 20 min with a constant current of 1 A. After treatment, part of the MAO covered samples treated by silicate electrolyte (MAO-Si) and sodium aluminate electrolyte (MAO-Al) were washed with deionized water and ethanol; another part of the samples (MAO-Si-P) were polished, and then dried in air for 24 h. Deionized water was used in all the experimental processes.

2.2 Fabrication of MAO/LDHs films

The MAO/LDHs films were prepared by an *in-situ* growth on the MAO covered samples. Zn $(NO_3)_2 \cdot 6 H_2O$ (0.05 M) and NH_4NO_3 (0.3 M) were dissolved in 300 ml deionized water, 1% ammonia was then added to the solution to adjust the pH value to 6.4. The MAO-Si sample was then vertically placed in the solution at 70 °C for 10 min, 30 min, 1 h, 6 h, 12 h and 24 h; the MAO-Al and MAO-Si-P samples were vertically placed in the solution at 70 °C for1 h, followed by rinsing with deionized water and ethanol and drying at 60 °C for 6 h.

2.3. Characterization

The surface morphology of the as-synthesized samples was characterized by scanning electron microscope (SEM, JEOL JSM-7800) at the voltage of 20 kV, and the chemical composition was investigated by energy dispersive spectroscopy (EDS). Crystallographic structures of the surface samples were examined by glancing angle X-ray diffraction (GAXRD, rigaku Ultima IV) at a glancing angle of 1° using Cu Kα_1 (λ=0.154 nm) radiation. LDH layers growth behavior was in-situ investigated by open circuit potential in electrochemical workstation system (Wuhan Corrtest Instruments Company, CS350) in a three electrode cell consisting of a saturated calomel reference electrode (SCE), a platinum foil counter electrode and the working electrode (exposed area of 1 cm^2).

3. RESULTS AND DISCUSSION

3.1. Growth behavior of LDHs layer on MAO sample

SEM micrographs of MAO-Si sample covered by LDHs layers for different growth times are shown in Fig.1. There are no LDH nanoplatelets observed on the surface of MAO film after 10 min (Fig. 1a) or 30 min (Fig. 1b) of growth. For the sample of 2 h growth, some LDHs nanoplatelets began

to form in the discharge hole and some areas on the surface. After growing for 6 h, the LDH nanoplatelets were vertically covered on most areas of the MAO film. Subsequently, the nanoplatelets become larger and thicker to form more uniform and dense layers and cover the complete range of the MAO surface after 12 h and 24 h of growth. Fig. 2 displays the growth schematic of the MAO/LDHs composite film, which showed the LDH layers grew vertically on the MAO film. In addition, the NO_3^- anions in LDH layers can be exchanged by inhibitor anions (such as vanadium acid-ions) for active protection via an anion exchange process.
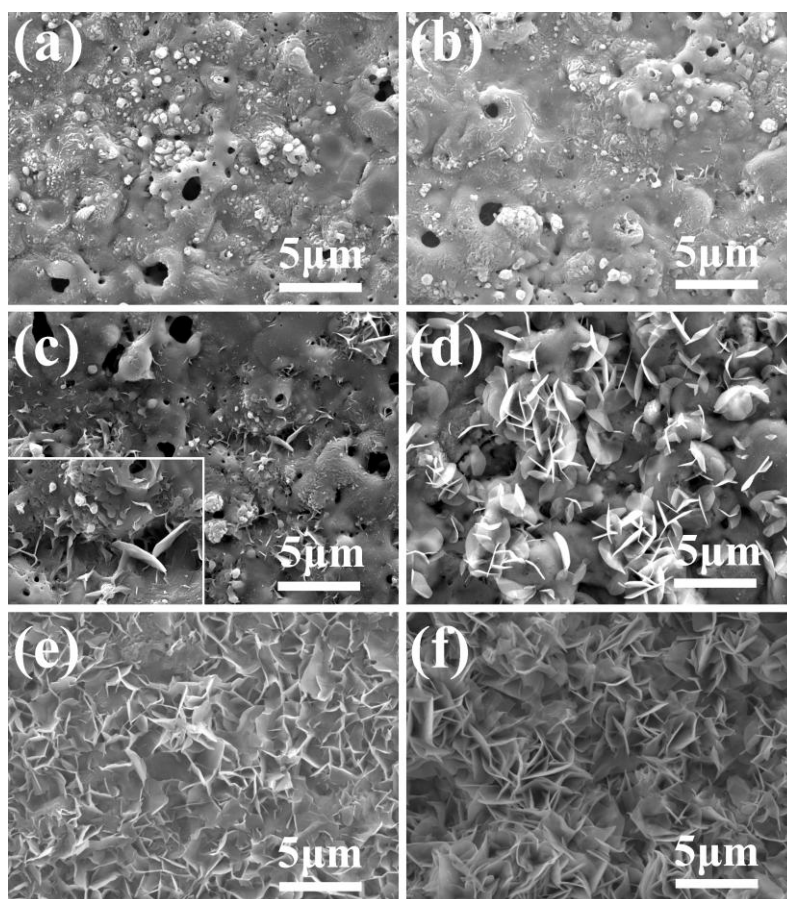

Figure 1. SEM micrographs of MAO-Si sample covered by LDHs layers for growth times of (a) 10min, (b) 30min, (c) 2h, (d) 6h, (e) 12h and (f) 24h. (The inset in part c is high resolution SEM image of the pores of MAO-Si film)

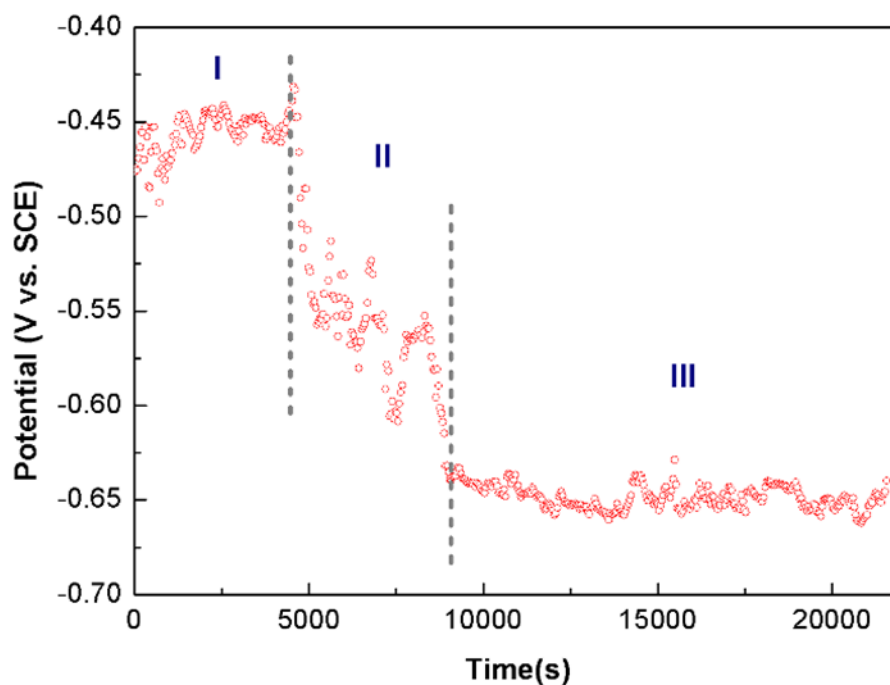**Figure 2.** The schematic of growth process of the MAO/LDHs composite film.

Figure 3. Potential vs. time curve during the formation of LDHs layers on MAO-Si sample in LDHs-growth solution.

In order to study the formation process of LDHs layer, the open circuit potential (OCP) of the MAO sample exposed to the LDHs-growth solution was investigated by E–T curves (Fig. 3) combined with the SEM morphologies observation. It is observed that the open potential (OCP) of the MAO sample in LDHs-growth solution is roughly divided into three stages: slow growth (I), rapid reduction (II), steady growth (III), as shown in Fig.1. In the initial stage of 0 ~ 2 hours immersion, the OCP of MAO sample grows very slowly, corresponding to the growth of LDH nanoplatelets in the MAO coating pores. The OCP of MAO sample rapidly decreases in the second stage of 2 ~ 6 hours immersion, corresponding to the linear growth of LDH nanoplatelets on the surface of MAO coating. The OCP value in stage III (6 ~ 24 h) reaches to a stable level, indicating that the LDH nanoplatelets grow denser on the surface of MAO coating.

However, it is found that the LDH layers are not uniform in the prophase stage from the SEM diagram (Fig.1), so we discussed the influence of MAO coating on LDH layers growth in two aspects.

3.2. The influence of microstructure and Si element of MAO coating

At the initial stage of LDH layers growth, some of LDHs nanoplatelets were preferentially formed on the micro-pores/-cracks, as shown in Fig. 4. The defects of micro-pores/-cracks are the penetration channels of corrosive ions to aluminum alloy substrate. Therefore, the preferred way of growth is in favor of MAO coating repair to improve the corrosion resistance of aluminum alloy surface, as we have discussed in previous studies [21]. On the top of MAO layer, these micro-pores were filled with hexagonal LDHs microcrystals, ensuring partial healing of the pores and providing an

effective corrosion inhibition. This unique microstructure of MAO coating effect on LDH nanoplatelets growth is also consistent with the results of Kuznetsov and Mohedano [22-23]. They found that the formation of LDHs strongly depended on the structure and composition of MAO layers. The synthesis of LDH layer could be explained by the following chemical reaction [24]:
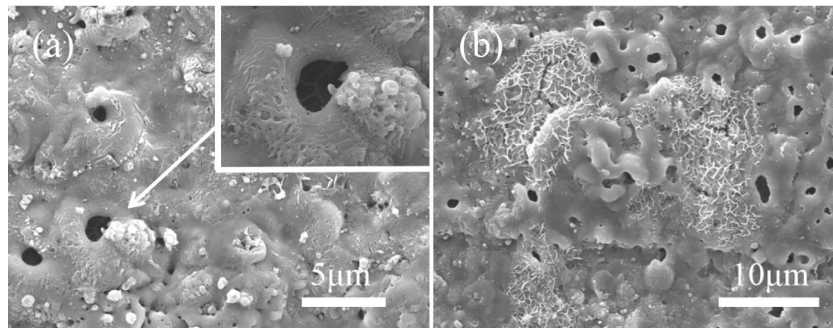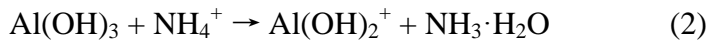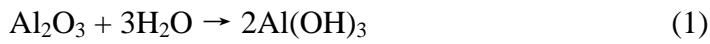
$$Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3 \qquad (1)$$
$$Al(OH)_3 + NH_4^+ \rightarrow Al(OH)_2^+ + NH_3 \cdot H_2O \qquad (2)$$
$$Zn(OH)^+ + Al(OH)_2^+ + 2NO_3^- \rightarrow LDH-NO_3 \qquad (3)$$

Figure 4. SEM images of LDHs/MAO films with micro-pores (a) and micro-cracks (b).
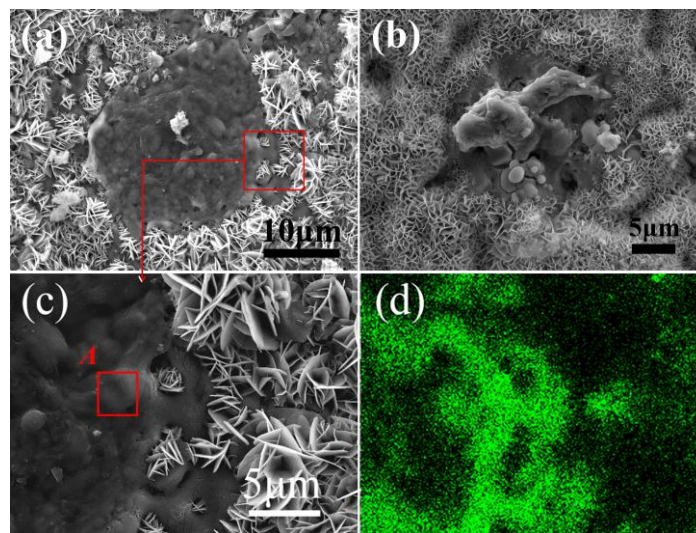

Figure 5. SEM and EDS-mapping images of some area without the growth of LDH nanoplatelets.

Table 1. EDS analysis of the area without LDH growing.

Element	Atomic%
C	40.09
N	8.04
O	28.04
Al	6.73
Mg	0.16
Si	14.18
Zn	2.76

In addition, it was found that some area are still not covered LDH nanoplatelets when the LDH layers grew to the later stage (24 h), as shown in Fig. 5. Fig. 5a and 5b present some small area of MAO surface had no LDH layers formation after 24 h of growth, but surrounded by full of LDH nanoplatelets. Mohedano [23] found that the growth of LDH mainly depended on the amount of $Al(OH)_2^+$. Thus, the distribution of Si element would have effect on the formation of LDHs. Fig. 5d is the Si element distribution of Fig. 5c, showing that the Si content of area without LDH nanoplatelets growth is much higher than that of LDH-covered area from the EDS analysis. This is indicating that the presence of Si on MAO coating could inhibit the grain nucleation and growth process of LDH nanoplatelets. The EDS analysis of A region (Table 1) showed that the content of Si elements is 14.18%, and the presence of Zn element may be due to the coverage of Zn in the solution on the surface of the A region, but the Si elements inhibited the nucleation and growth of the LDHs grains. We found that the content of Si elements is not high from the EDS analysis of Fig. 5b, so it may be because its unique structure affects the growth of LDH nanoplatelets.

When discussing the source of Si elements, we found that the amount of Si in the 2024 aluminum alloy is very small, and the growth behavior of LDH layers is not affected. Therefore, the Si elements are only mainly from the preparation of MAO coating in the sodium silicate electrolyte. Si elements in the preparation of MAO coating could react with Al of aluminum alloy substrate to generate compounds, may also be spewed by MAO of the melt the packages, resulting in the high content of Si on the prepared MAO coating. Therefore, we use the following two methods to investigate this effect on LDH growth behavior by changing the electrolyte without Si and polishing the surface to remove Si.
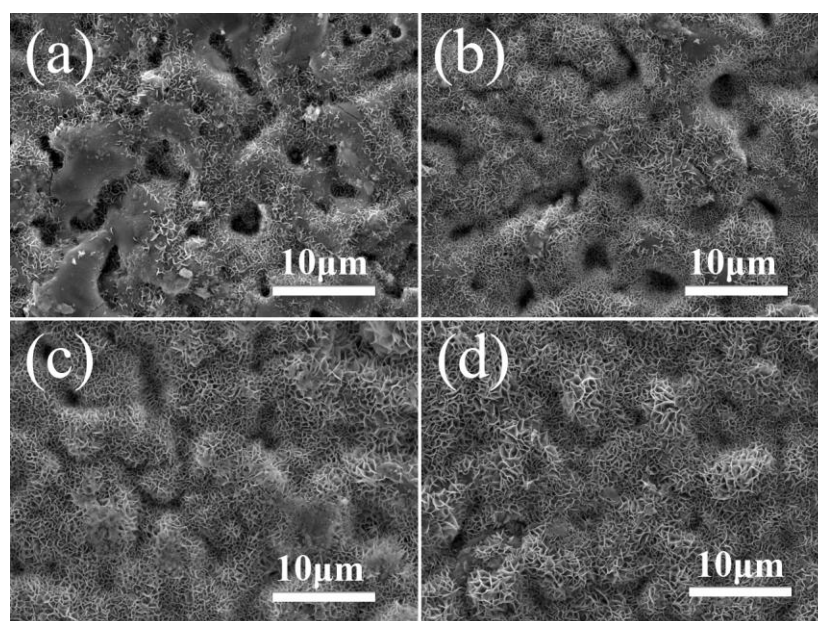

Figure 6. SEM images of the LDH growth behavior on MAO coating prepared in sodium aluminate electrolyte: (a) 1h; (b) 6h; (c) 12h; (d) 24h.

The first approach to remove Si on the MAO surface is to change the sodium silicate electrolyte to sodium aluminate electrolyte. Fig. 6 shows the growth behavior of LDH layers on MAO coating prepared in sodium aluminate electrolyte. Fig. 6a presents a large number of small LDH nanoplatelets formed on the MAO coating after 1 h growth. Only some of the protruding parts are not covered by LDHs. Compared with the MAO coating prepared in sodium silicate electrolyte, the coating prepared in sodium aluminate is more conducive to the growth of LDH layers. LDH nanoplatelets only grow in the pores of the MAO-Si coating after 2h (Fig.1c). It is found that the bulges have been also uniformly covered by LDHs nanoplatelets after 6 h of growth, as shown in Fig. 6. During 12 h and 24 h of growth (Fig. 6c and 6d), it is observed that LDH layers grow more uniformly over time with the holes filled more smoothly and the nanoplatelets became larger.
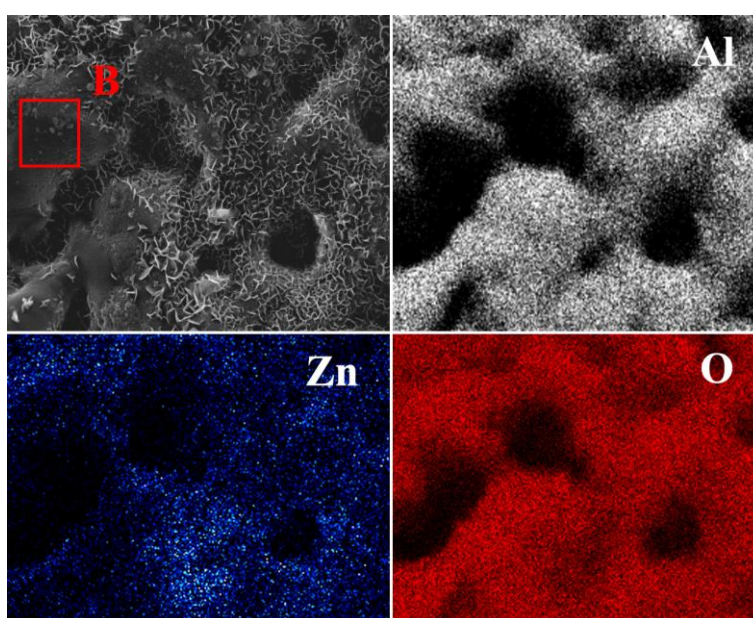

Figure 7. EDS-mapping images of the LDH layers on MAO-Al coating.

Table 2. EDS analysis of the LDH layers on MAO-Al coating.

Element	Atomic%
C	10.34
O	47.65
Al	40.45
Zn	1.56

EDS-mapping analysis of the MAO-Al surface after 1 h of LDHs growth is displayed in Fig. 7. It can be found that the amounts of Al, O and Zn are large with no Si element detected. Al, O and Zn elements are derived from LDH layers or MAO coating. Without the use of silicate electrolytes, the content of Si is so small that it will not affect the growth of LDHs. The elemental analysis of the B

region is further demonstrated that there is no Si element present in the region without LDHs growth, as shown in Table 2.
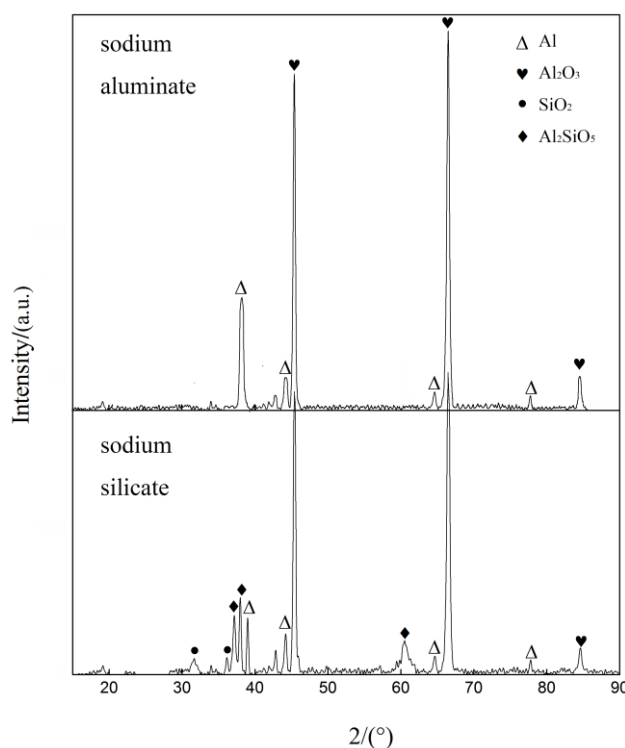

Figure 8. XRD analysis of MAO samples prepared by silicate and aluminate electrolyte.
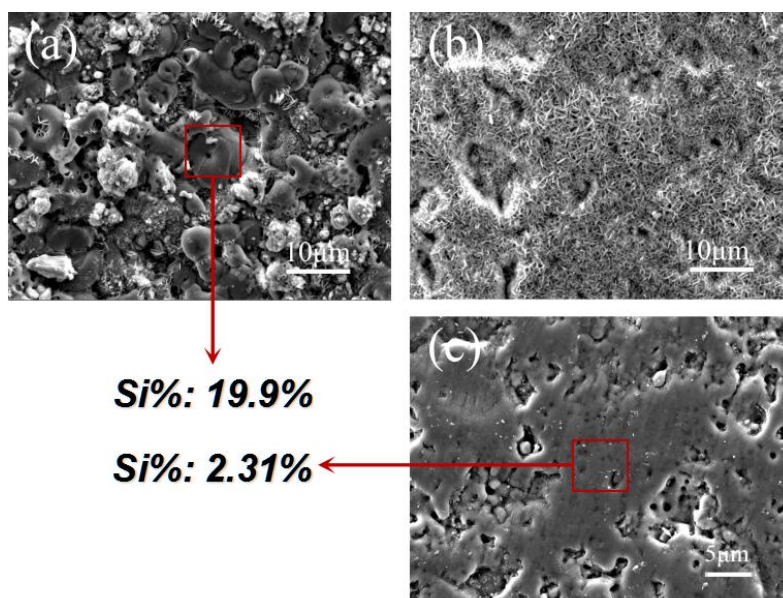

Figure 9. SEM images and EDS analysis of MAO-Si surface with non-polishing (a) and after polishing (c); surface morphology of LDHs layer on polished MAO-Si sample after 1h growth (b).

XRD patterns of the two MAO coating samples prepared in different electrolyte are showed in Fig. 8. The sample prepared in silicate electrolyte contained SiO_2 and silicon compound [25-27]. However, no silica phase appeared in the sample prepared in sodium aluminate electrolyte, and only detecting the Al_2O_3 phase and Al matrix. In addition, the higher content of Al_2O_3 in the sample prepared in sodium aluminate solution indicates that the Al element in sodium aluminate electrolyte is capable to promote the growth of MAO coating, obtaining more compact MAO coating and improved surface performance of aluminum alloy.

The second aspect was the polishing of MAO coating prepared in sodium silicate solution to remove the Si elements existed on the surface of MAO coating, which can providing a non-Si MAO surface to allow better growth of LDH layers. Fig. 9a and 9c showed the content of Si elements on the surface of MAO-Si sample with non-polishing and after polishing, respectively. The EDS data show that the content of Si on the surface of MAO-Si sample is greatly reduced after polishing. Fig. 8b shows the surface morphology of LDHs layer on polished MAO-Si sample after 1h growth. It can be seen that LDH nanoplatelets grow more uniformly and densely on MAO-Si sample after polishing compared with the growth behavior on MAO-Si sample.

Thus, it can be concluded that the microstructure, surface composition and Si content of MAO film have a significant effect on the growth behavior of LDHs layer. LDHs grains can be preferentially grown at the micro-pores or micro-cracks of the ceramic layer to provide effective film repairs. At the same time, the silicon-containing phase on the surface of the MAO film significantly inhibits the nucleation and growth of the LDHs grains on the surface of the MAO film.

4. CONCLUSION

This research investigated the growth behavior of LDH layers on MAO-coated aluminum alloy, focusing on two factors: microstructure and Si amount on the surface of MAO ceramic layer. Firstly, LDHs grains are preferentially formed in/on the micro-pores/-cracks of MAO coating to provide effective film repairs. Meanwhile, the areas without LDH nanoplatelets contain high amount of Si element on the surface. Then, we use two methods to investigate this effect on LDH growth behavior by changing the electrolyte without Si and polishing the surface to remove Si. Compared with the MAO-Si coating, a large number of small LDH nanoplatelets are uniformly formed on the MAO-Al coating after 1 h growth. No Si element is detected on the MAO-Al coating, showing the MAO ceramic coating prepared in sodium aluminate is more conducive to the growth of LDH layers. In addition, the LDH nanoplatelets grow more uniformly and densely on MAO-Si sample after polish, because the content of Si on the surface of MAO-Si sample is greatly reduced.

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